

MIXED LIGAND COMPLEXES OF PLATINUM(0) CONTAINING DIPHOSPHINES

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Summary

The reaction of PtCl_2L (L = diphosphine) with the appropriate diphosphine L' in ethanol followed by reduction with aqueous sodium borohydride leads to either disproportionation to give mixtures of the bis(diphosphine) complexes PtL_2 and PtL'_2 or to the formation of the mixed ligand complex PtLL' depending on the diphosphines. Mixed ligand complexes are obtained when $\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$, $\text{L}' = \text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2$, *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{AsPh}_2$, $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$, *o*- $\text{Ph}_2\text{PC}_6\text{H}_4\text{PPh}_2$; and $\text{L} = (\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_{11})_2$, $\text{L}' = \text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2$, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$, *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$, (2*S*,3*S*)- $\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{PPh}_2$, (*R*)- $\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}_2\text{PPh}_2$. When $\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$, $\text{L}' = \text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ or *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$ the mixed ligand complexes are obtained but extensive disproportionation also occurs.

Introduction

Transition metal complexes of low symmetry can be useful in studies such as those involving asymmetric syntheses catalysed by metal complexes, and investigations of the electronic and steric effects of ligands on the reactivity and catalytic activity of transition metal complexes [1–5], and can provide valuable NMR information unattainable from symmetrical compounds [6]. We have recently reported the preparation of platinum(II) complexes with mixed unidentate phosphine ligands and have found that they have an extensive chemistry without disproportionation [1,2]. There have been relatively few reports, however, of platinum(0) complexes containing mixed phosphine ligands [6–8]. In this paper we wish to report our studies on the preparation of platinum(0) complexes containing mixed diphosphine ligands. Such complexes can additionally provide some insight into the effect of chelate ring size on reactivity and on NMR parameters.

The preparation of bis(diphosphine)platinum(0) complexes by the reduction of platinum(II) species is well known [9–11]. Thus $\text{Pt}(\text{dppe})_2$ ($\text{dppe} = \text{Ph}_2\text{P}-$

$(\text{CH}_2)_2\text{PPh}_2$) is prepared by the reduction of $\text{PtCl}_2(\text{dppe})$ with sodium borohydride in ethanol in the presence of excess dppe [9], while other complexes, PtL_2 (L = diphosphine), are prepared by reacting potassium tetrachloroplatinate with either sodium borohydride and the diphosphine L [11] (e.g. $\text{L} = \text{cis-Ph}_2\text{PCH=CHPPh}_2$) or with potassium hydroxide/ethanol and the diphosphine L ($\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, $n = 2-4$) [10]. There are, however, few reports of platinum(0) diphosphine complexes containing mixed ligands. Two such compounds are $\text{Pt}(\text{diop})(\text{dppe})$ ($\text{diop} = 2,3$ -isopropylidene-2,3-*trans*-dehydroxy-1,4-bis-(diphenylphosphino)butane), prepared by reacting $\text{Pt}(\text{diop})_2$ with dppe [7], and $\text{Pt}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\text{triphos})$ ($\text{triphos} = (\text{Ph}_2\text{PCH}_2)_3\text{CCH}_3$), in which triphos acts as a bidentate ligand [8].

Results

We have attempted to prepare mixed diphosphine platinum(0) complexes by initially refluxing $\text{PtCl}_2(\text{diphosphine})$ in ethanol with the appropriate diphosphine and then adding an aqueous solution of sodium borohydride to give the zerovalent complex. When this reaction is carried out using $\text{PtCl}_2(\text{dppm})$ ($\text{dppm} = \text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2$) and dppe, the ^{31}P NMR spectrum of the orange product shows two triplets (with platinum satellites) at $\delta -22.8$ ($^1J(\text{P-Pt})$ 3006 Hz) and 30.6 ($^1J(\text{P-Pt})$ 4063 Hz). This spectrum is consistent with the mixed diphosphine platinum(0) complex $\text{Pt}(\text{dppm})(\text{dppe})$. The signal at $\delta -22.8$ can be assigned to the dppm phosphorus atoms and that at 30.6 to the dppe phosphorus atoms. These chemical shifts are typical of chelated dppm and dppe respectively [12]. The magnitude of $^2J(\text{P-P})$ (45 Hz) is similar to that of the known complex $\text{Pt}(\text{diop})(\text{dppe})$ ($^2J(\text{P-P})$ 56 Hz) [7]. The complex $\text{Pt}(\text{dppm})(\text{dppe})$ is a relatively stable solid and can be stored for several weeks under a nitrogen atmosphere but decomposes in solution in benzene within a few hours even under nitrogen. The same product is also obtained by starting from $\text{PtCl}_2(\text{dppe})$ and dppm; however the ^{31}P NMR spectrum shows an additional peak at δ 30.6 ($^1J(\text{P-Pt})$ 3729 Hz) which can be assigned to $\text{Pt}(\text{dppe})_2$ by comparison with an authentic sample [9] (^{31}P NMR δ 30.2, $^1J(\text{P-Pt})$ 3728 Hz). In contrast to the reaction of $\text{PtCl}_2(\text{dppm})$ and dppe, the reaction of $\text{PtCl}_2(\text{dppm})$, $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ (= dppp) and sodium borohydride gives a yellow solid whose ^{31}P NMR spectrum shows a peak at $\delta -10.8$ ($^1J(\text{P-Pt})$ 3645 Hz) and a peak at 40.3 with complicated ^{195}Pt satellites ($^1J(\text{P-Pt})$ 4507 Hz). The signal at $\delta -10.8$ can be assigned to $\text{Pt}(\text{dppp})_2$ (^{31}P NMR $\delta -10.8$, $^1J(\text{P-Pt})$ 3649 Hz) by preparing $\text{Pt}(\text{dppp})_2$ from the reaction of $\text{PtCl}_2(\text{dppp})$, dppp and sodium borohydride. The formation of $\text{Pt}(\text{dppp})_2$ suggests that disproportionation has occurred.

To identify the other product, $\text{PtCl}_2(\text{dppm})$ and one equivalent of dppm in ethanol were reacted with aqueous sodium borohydride. The resulting red complex shows a single peak in its ^{31}P NMR spectrum with complicated satellites (δ 40.6, $^1J(\text{P-Pt})$ 4507 Hz). Its spectrum is identical to that of the second product in the reaction of $\text{PtCl}_2(\text{dppm})$, dppp and sodium borohydride. The chemical shift of the signal in its ^{31}P NMR spectrum suggests that chelating dppm is not present [12,13]. The value of $^1J(\text{P-Pt})$ is consistent with three-coordinate platinum(0) [14,15] and the complicated nature of the satellites suggests a binuclear species. The complex is most probably the recently reported $\text{Pt}_2(\text{dppm})_3$ [16,17]. The relatively insoluble $\text{Pt}(\text{dppp})_2$ can be separated pure from the reaction product by fractional recrystallization from

benzene. The complexes, $\text{Pt}(\text{dppp})_2$ and $\text{Pt}_2(\text{dppm})_3$, are also obtained in the reaction of $\text{PtCl}_2(\text{dppp})$, dppm and sodium borohydride. The reaction of $\text{PtCl}_2(\text{dppm})$ and $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ (= dppb) (or $\text{PtCl}_2(\text{dppb})$ and dppm) with sodium borohydride gives a yellow product, the ^{31}P NMR spectrum of which shows two singlets at δ 40.7 ($^1J(\text{P-Pt})$ 4507 Hz) and δ -0.7 ($^1J(\text{P-Pt})$ 3754 Hz). The signal at δ 40.7 can be identified as $\text{Pt}_2(\text{dppm})_3$ while that at δ -0.7 can be identified as $\text{Pt}(\text{dppb})_2$ by comparison with authentic $\text{Pt}(\text{dppb})_2$ (^{31}P NMR δ -0.3, $^1J(\text{P-Pt})$ 3740 Hz) prepared from the reaction of $\text{PtCl}_2(\text{dppb})$ and dppb with sodium borohydride.

The bis(diphenylphosphino)ethane complex $\text{PtCl}_2(\text{dppe})$ reacts with dppp and sodium borohydride to give a yellow solid. The ^{31}P NMR spectrum of this solid shows two singlets at δ 31.1 ($^1J(\text{P-Pt})$ 3730 Hz) and δ -9.9 ($^1J(\text{P-Pt})$ 3647 Hz) assignable to $\text{Pt}(\text{dppe})_2$ and $\text{Pt}(\text{dppp})_2$ by comparison with the ^{31}P NMR spectra of authentic samples of these complexes. The relatively insoluble $\text{Pt}(\text{dppp})_2$ can be separated from the reaction product by fractional recrystallization from benzene. The reaction of $\text{PtCl}_2(\text{dppp})$ and dppe with sodium borohydride proceeds similarly. The ^{31}P NMR spectrum of the product of the reaction of $\text{PtCl}_2(\text{dppe})$ and dppb (or $\text{PtCl}_2(\text{dppb})$ and dppe) with sodium borohydride shows two triplets at δ 24.2 ($^1J(\text{P-Pt})$ 3477 Hz) and 3.3 ($^1J(\text{P-Pt})$ 3955 Hz). This spectrum is consistent with the tetrahedral platinum(0) complex $\text{Pt}(\text{dppe})(\text{dppb})$. The triplets at δ 24.2 and 3.3 can be assigned to the dppe and dppb phosphorus atoms respectively by comparison with known compounds containing chelating dppe and dppb [12]. Molecular weight measurements suggest that the complex is largely monomeric in solution. The complex is stable as a solid when stored under nitrogen but decomposes slowly, over a few days, in benzene under nitrogen. Bis(diphenylphosphino)benzene (dppbe) reacts with $\text{PtCl}_2(\text{dppe})$ and sodium borohydride to give the mixed ligand complex $\text{Pt}(\text{dppe})(\text{dppbe})$ as shown by its ^{31}P NMR spectrum which shows two triplets with ^{195}Pt satellites at δ 31.3 ($^1J(\text{P-Pt})$ 3676 Hz) and 33.1 ($^1J(\text{P-Pt})$ 3724 Hz). These signals can be assigned to the dppe and dppbe phosphorus atoms respectively. Similarly *cis*-bis(diphenylphosphino)ethylene (*cis*- dppe) reacts with $\text{PtCl}_2(\text{dppe})$ and sodium borohydride to give $\text{Pt}(\text{dppe})(\text{cis-dppe})$ as a yellow solid whose ^{31}P NMR spectrum shows two triplets with ^{195}Pt satellites at δ 30.2 ($^1J(\text{P-Pt})$ 3766 Hz) and 34.8 ($^1J(\text{P-Pt})$ 3744 Hz) assignable to the dppe and *cis*- dppe phosphorus atoms respectively. A mixed ligand complex is also obtained from the reaction of $\text{PtCl}_2(\text{dppe})$, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{AsPh}_2$ (= arphos) and sodium borohydride. The ^{31}P NMR spectrum of $\text{Pt}(\text{dppe})(\text{arphos})$ shows a doublet at δ 33.6 ($^1J(\text{P-Pt})$ 4093 Hz) assignable to the dppe phosphorus atoms and a triplet at 39.4 ($^1J(\text{P-Pt})$ 4270 Hz) assignable to the arphos phosphorus atom.

Reaction of $\text{PtCl}_2(\text{dppp})$ and dppb (or $\text{PtCl}_2(\text{dppb})$ and dppp) with sodium borohydride results in about 50% disproportionation to give $\text{Pt}(\text{dppp})_2$, $\text{Pt}(\text{dppb})_2$ and the mixed ligand complex $\text{Pt}(\text{dppb})(\text{dppp})$ as shown by the ^{31}P NMR spectrum of the product. The spectrum shows two triplets with ^{195}Pt satellites at δ -15.1 ($^1J(\text{P-Pt})$ 3561 Hz) and 2.7 ($^1J(\text{P-Pt})$ 3862 Hz) for the mixed ligand complex. The triplets are assignable to the dppp and dppb phosphorus atoms respectively. The complex $\text{Pt}(\text{dppb})(\text{dppp})$ could not be separated from the bis(diphosphine)-platinum(0) compounds. When $\text{PtCl}_2(\text{dppb})$ is reacted with *cis*-bis(diphenylphosphino)ethylene (*cis*- dppe) and sodium borohydride an orange-yellow solid is obtained. The ^{31}P NMR spectrum of this product shows two singlets (with ^{195}Pt

satellites) at δ 0.01 ($^1J(\text{P-Pt})$ 3745 Hz) and 34.2 ($^1J(\text{P-Pt})$ 3778 Hz) assignable to $\text{Pt}(\text{dppb})_2$ (see Table 1) and $\text{Pt}(\text{cis-dppe})_2$ [11] (^{31}P NMR: δ 34.2 ($^1J(\text{P-Pt})$ 3778 Hz)) respectively and two triplets (also with ^{195}Pt satellites) at δ 5.8 ($^1J(\text{P-Pt})$ 3983 Hz) and 28.4 ($^1J(\text{P-Pt})$ 3606 Hz) assignable to the dppb and *cis*-dppe phosphorus atoms respectively of a mixed ligand species. As shown by ^{31}P NMR, approximately 50% disproportionation has occurred to give the bis(diphosphine)platinum(0) complexes which could not be separated from the mixed ligand complex.

The bis(dicyclohexylphosphino)ethane (dcpe) complex $\text{PtCl}_2(\text{dcpe})$ reacts with a number of diphosphine and sodium borohydride to give mixed ligand complexes. With dppm an orange-yellow solid is obtained. On recrystallization from benzene the orange-yellow complex $\text{Pt}(\text{dcpe})(\text{dppm})$ crystallizes out. The ^{31}P NMR spectrum (Fig. 1) of this complex shows the expected A_2X_2 pattern (with ^{195}Pt satellites) (Table 1). The triplet at δ -33.2 is due to chelated dppm [12] while that at 53.0 can be assigned to the dcpe phosphorus atoms by comparison with the ^{31}P NMR spectrum of $\text{PtCl}_2(\text{dcpe})$ (^{31}P NMR (in CDCl_3): δ 64.1, $^1J(\text{P-Pt})$ 3577 Hz). The benzene filtrate yields a yellow solid whose ^{31}P NMR spectrum (in $\text{C}_6\text{D}_6/\text{C}_2\text{H}_5\text{OH}$ at 161.98 MHz) shows two ^{31}P NMR signals at δ 66.4 (d, $^2J(\text{P-P})$ 296, $^1J(\text{P-Pt})$ 2238 Hz) and -40.5 (d, $^2J(\text{P-P})$ 296, $^1J(\text{P-Pt})$ 1835 Hz). For both signals, the magnitude of $^1J(\text{P-Pt})$ is consistent with a platinum(II) complex containing *trans* phosphines [14,15]. The value of $^2J(\text{P-P})$ is typical of coupling between inequivalent *trans* phosphines in a platinum(II) complex [18,19]. Thus the complex is probably $[\text{Pt}(\text{dcpe})(\text{dppm})]^{2+}$ and its presence is due to incomplete reduction. The chemical shifts of the signals at δ 66.4 and -40.5 are consistent with chelated dcpe (by comparison with $\text{PtCl}_2(\text{dcpe})$ ($\delta(^{31}\text{P})$ 64.1) and dppm [12] respectively. Mixed ligand complexes, $\text{Pt}(\text{dcpe})(\text{L})$ are also obtained when $\text{L} = \text{cis-dppe}$, dppbe, (*R*)- $\text{Ph}_2\text{PCH}(\text{CH}_3)\text{CH}_2\text{PPh}_2$ (prophos) and (2*S*,3*S*)- $\text{Ph}_2\text{P}(\text{CH}(\text{CH}_3))_2\text{PPh}_2$ (chiraphos). For $\text{L} = \text{dppbe}$ the mixed ligand complex $\text{Pt}(\text{dcpe})(\text{dppbe})$ is obtained in a very low yield and could not be obtained pure. The low yield is due to incomplete reaction of $\text{PtCl}_2(\text{dcpe})$ and dppbe. For $\text{L} = \text{chiraphos}$ the mixed ligand species $\text{Pt}(\text{dcpe})(\text{chiraphos})$ is obtained as shown by its ^{31}P NMR spectrum which shows two complex multiplets centered at δ 45.1 and 29.5 due to the dcpe and chiraphos [20,21] phosphorus atoms respectively. The multiplets are not sufficiently resolved to permit a detailed analysis of the spectrum. For $\text{L} = \text{prophos}$, the mixed ligand complex $\text{Pt}(\text{dcpe})(\text{prophos})$ is obtained. The ^{31}P NMR spectrum of this complex shows signals due to the four inequivalent phosphorus atoms at δ 46.0 ($^1J(\text{P-Pt})$ 3596,

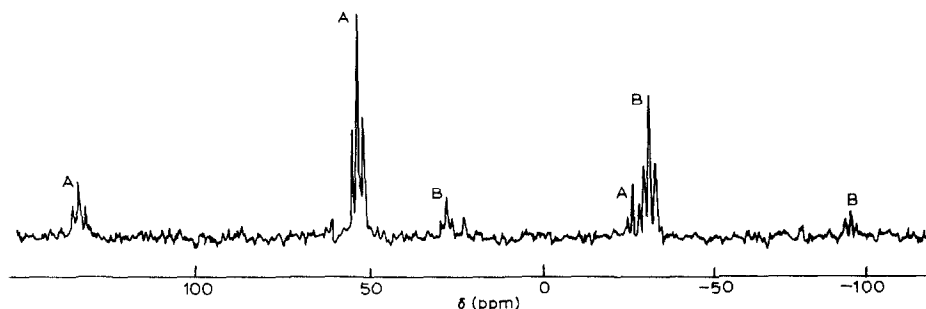


Fig. 1. ^{31}P $\{^1\text{H}\}$ NMR spectrum of $\text{Pt}(\text{dcpe})(\text{dppm})$ in C_6D_6 (A = dcpe, B = dppm).

$^2J(\text{Pdcpe-Pdcpe})$ 80.9, $^2J(\text{Pdcpe-Pprophos})$ 82.2, 31.9 Hz) and δ 44.5 ($^1J(\text{P-Pt})$ 3608, $^2J(\text{Pdcpe-Pprophos})$ 30.35, 84.8 Hz) due to the dcpe phosphorus atoms and at δ 29.1 ($^1J(\text{P-Pt})$ 3660 Hz, $^2J(\text{Pprophos-Pprophos})$ 72.45 Hz, $^2J(\text{dcpe-prophos})$ 31.9, 84.8 Hz) and 11.4 ($^1J(\text{P-Pt})$ 3645 Hz, $^2J(\text{Pprophos-dcpe})$ 82.2, 30.35 Hz) due to the prophos phosphorus atoms [20,21].

The acetylenic phosphine complex $\text{Pt}_2\text{Cl}_4(\text{dppa})_2$ ($\text{dppa} = \text{Ph}_2\text{PC}\equiv\text{CPh}_2$) [22] reacts with dppe and sodium borohydride to give a mixture of the mixed ligand complex $(\text{dppe})\text{Pt}(\text{Ph}_2\text{PC}\equiv\text{CPh}_2)_2\text{Pt}(\text{dppe})$ and the bis(phosphine) complex $\text{Pt}(\text{dppe})_2$ as shown by the ^{31}P NMR spectrum of the product which shows two triplets (with ^{195}Pt satellites) at δ 29.4 ($^1J(\text{P-Pt})$ 3661 Hz) and -15.0 ($^1J(\text{P-Pt})$ 4008 Hz) due to the dppe and acetylenic phosphine phosphorus atoms respectively and a singlet at δ 34.0 due to $\text{Pt}(\text{dppe})_2$. Some decomposition (presumably to platinum metal) also occurs in this reaction. When $\text{Pt}_2\text{Cl}_4(\text{Ph}_2\text{PC}\equiv\text{CPh}_2)_2$ is reacted with dppp the only isolable product is $\text{Pt}(\text{dppp})_2$, identifiable from its ^{31}P NMR spectrum. A similar reaction using dcpe resulted in extensive decomposition.

We have also attempted to prepare, by a reaction similar to that used for the preparation of mixed ligand diphosphine complexes, zerovalent platinum complexes containing a bidentate phosphine and unidentate phosphines. Thus $\text{PtCl}_2(\text{dppe})$ reacts with tricyclohexylphosphine and sodium borohydride to give, as shown by ^{31}P NMR, a mixture of $\text{Pt}(\text{dppe})_2$ ($\delta(\text{P})$ 30.4, $^1J(\text{P-Pt})$ 3728 Hz) and $\text{PtH}_2(\text{P}(\text{C}_6\text{H}_{11})_3)_2$ ($\delta(\text{P})$ 52.7, $^1J(\text{P-Pt})$ 2874 Hz, $\nu(\text{Pt-H})$ 1710 cm^{-1}) [23] while $\text{PtCl}_2(\text{PPh}_3)_2$ reacts with dppe and sodium borohydride to give $\text{Pt}(\text{dppe})_2$. Similarly $\text{PtCl}_2(\text{PMe}_2\text{Ph})_2$ reacts with dppp and sodium borohydride to give $\text{Pt}(\text{dppp})_2$.

Discussion

The reaction of PtCl_2L ($\text{L} = \text{diphosphine}$), one equivalent of another diphosphine, L' , and sodium borohydride presumably proceeds by the initial formation of cationic complexes such as $[\text{PtLL}']^{2+}$ which are then reduced by sodium borohydride to the zerovalent platinum compounds PtLL' . This is supported by the preparation of $[\text{Pt}(\text{dppe})_2]^{2+}$ by the reaction of $\text{PtCl}_2(\text{dppe})$ and dppe [24] and by the production of $[\text{Pt}(\text{dcpe})(\text{dppm})]^{2+}$ in the reaction of $\text{PtCl}_2(\text{dcpe})$, dppm and sodium borohydride.

The factors determining whether mixed ligand complexes form or disproportionation occurs are not clear. It might be expected that due to the strained nature of the chelated dppm ligand it would be reluctant to form mixed ligand complexes. However, $\text{Pt}(\text{dppe})(\text{dppm})$ and $\text{Pt}(\text{dcpe})(\text{dppm})$ can be prepared. The less strained dppp does not, however, form a mixed ligand complex with either dppm or dppe, perhaps because the relatively insoluble $\text{Pt}(\text{dppp})_2$ forces disproportionation. Dcpe readily forms mixed ligand complexes with dppm, dppe and other diphosphines with five-membered chelate rings but not with dppp or dppb, perhaps because the bulky cyclohexyl groups prevent formation of mixed ligand complexes containing the larger chelate ring diphosphines.

The values of $\delta(\text{P})$ for the mixed ligand complexes are similar to those observed for other diphosphine complexes and show the same dependence on chelate ring size [12,19]. Thus $\delta(\text{P})$ increases in the order $\delta(\text{P}(\text{dppm})) < \delta(\text{P}(\text{dppp})) < \delta(\text{P}(\text{dppb})) < \delta(\text{P}(\text{dppe}))$ due to the ring contribution to the phosphorus chemical shift [12].

The values of $^1J(\text{P-Pt})$ for the mixed ligand complexes, PtLL' , show a number of interesting trends. The value of $^1J(\text{P-Pt})$ (Table 1) for the dppe phosphorus atoms of

the mixed ligand complexes $\text{Pt}(\text{dppe})\text{L}$ is very dependant on the diphosphine, L. The value of the coupling constant changes from 3477 to 4063 Hz, increasing in the order $\text{L} = \text{dppb} < \text{dcpe} \approx \text{dppe} < \text{dppm}$ i.e. in decreasing size of the chelate ring of the diphosphine L. It is apparent from Table 1 that the value of $^1J(\text{P-Pt})$ for the mixed ligand diphosphine complexes PtLL' is larger for the phosphorus atoms of the diphosphine with the larger chelate ring size. The magnitude of $^1J(\text{P-Pt})$ is generally thought to be dominated by the Fermi contact term and can be expressed as in eq. 1 where $[S_{\text{P}}(0)]$ and $[S_{\text{Pt}}(0)]$ are the s -electron density of phosphorus and platinum respectively measured at the nucleus and $\pi(\text{PPt})$ [25] is the mutual polarizability [26–31].

$$^1J(\text{PPt}) = (\text{constant})(\gamma_{\text{P}}\gamma_{\text{Pt}})[S_{\text{P}}(0)]^2[S_{\text{Pt}}(0)]^2\pi(\text{PPt}) \quad (1)$$

Saito et al. [28] have shown that variations in $[S_{\text{P}}(0)]$ and $[S_{\text{Pt}}(0)]$ are unimportant to the magnitude of $^1J(\text{PPt})$ and that $^1J(\text{PPt})$ is primarily dependant on the mutual polarizability term $\pi(\text{PPt})$. As mutual polarizability is related to the s -orbital bond order of the P–Pt bond, the increasing magnitude of $^1J(\text{P-Pt})$ for the dppe phosphorus atoms of the complexes $\text{Pt}(\text{dppe})\text{L}$ as the size of the chelate ring of L is decreased can be related to an increase in the s -bond character of the Pt–P bonds of the dppe. This is the result of the dppe phosphorus atoms getting a greater share of the platinum $6s$ valence orbital due to the decreased ability of the phosphorus atoms of L to overlap with the platinum $6s$ orbital as the chelate ring size of L decreases. Thus for a complex PtLL' the phosphorus atoms of the diphosphine with the larger chelate ring size will have the greater magnitude of $^1J(\text{P-Pt})$ as it is best able to compete for overlap with the platinum $6s$ orbital as its P–Pt–P bond angle most

TABLE 1
 $^{31}\text{P}\{^1\text{H}\}$ NMR DATA FOR PLATINUM(0) COMPLEXES ^a

Compound	$\delta(\text{P}_{\text{A}})$ ^b	$^1J(\text{Pt-P}_{\text{A}})$	$\delta(\text{P}_{\text{B}})$ ^b	$^1J(\text{Pt-P}_{\text{B}})$	$^2J(\text{P}_{\text{A}}-\text{P}_{\text{B}})$
$\text{Pt}_2(\text{dppm})_3$ ^c	40.6	4507			
$\text{Pt}(\text{dppe})_2$ ^d	30.2	3728			
$\text{Pt}(\text{dppp})_2$	– 10.8	3648			
$\text{Pt}(\text{dppb})_2$	– 0.3	3740			
$\text{Pt}(\text{cis-dppe})_2$	34.2	3778			
$\text{Pt}(\text{dppm})(\text{dppe})$	– 22.8	3006	30.6	4063	45
$\text{Pt}(\text{dppm})(\text{dcpe})$	– 33.2	2913	53.0	3933	43
$\text{Pt}(\text{dppe})(\text{dcpe})$	22.5	3665	44.7	3607	59
$\text{Pt}(\text{dppe})(\text{cis-dppe})$	30.2	3766	34.8	3744	60
$\text{Pt}(\text{dppe})(\text{dppbe})$	31.3	3676	33.1	3724	54
$\text{Pt}(\text{dppe})(\text{arphos})$	33.6	4093	39.4	4270	78
$\text{Pt}_2(\text{dppe})_2(\text{dppa})_2$	29.4	3661	– 15.0	4008	55
$\text{Pt}(\text{dppe})(\text{dppb})$	24.2	3477	3.3	3955	56
$\text{Pt}(\text{dcpe})(\text{dppbe})$	43.4	3539	28.6	3695	61
$\text{Pt}(\text{dcpe})(\text{cis-dppe})$	43.1	3626	26.3	3682	54
$\text{Pt}(\text{dppb})(\text{dppp})$	2.7	3862	– 15.1	3561	48
$\text{Pt}(\text{dppb})(\text{cis-dppe})$	5.8	3983	28.4	3606	56

^a 161.9 MHz in C_6D_6 , δ in ppm to high frequency of ext. H_3PO_4 , J in Hz. ^b P_{A} first mentioned phosphine, P_{B} last mentioned ^c ^{195}Pt satellites are a superposition of $\text{AA}'\text{A}'''\text{A}'''\text{A}'''\text{A}'''\text{XX}'$ and $\text{AA}'\text{A}'''\text{A}'''\text{A}'''\text{X}$ spin systems cf. ref. 16. ^d $\delta(\text{Pt})$ – 3794 (quintet) in C_6D_6 .

TABLE 2
ELEMENTAL ANALYSES

Compound	Analyses (Found (calcd.) (%))		MW ^a
	C	H	
Pt(dppm)(dppe)	62.27 (62.66)	4.71 (4.71)	10.41 (977.5)
Pt(dppm)(dcpe)	61.05 (61.16)	7.00 (6.99)	^b
Pt(dppe)(dppb)	63.32 (63.59)	5.34 (5.13)	860 (1019.8)
Pt(dppe)(dcpe)	60.74 (61.46)	6.75 (7.14)	^c
Pt(dppe)(dppbe)	64.91 (64.68)	4.85 (4.64)	1029 (1039.8)
Pt(dppe)(<i>cis</i> -dppe)	63.23 (63.10)	4.88 (4.67)	1185 (989.8)
Pt(dppe)(arphos)	60.67 (60.30)	4.70 (4.66)	1152 (1035.7)
Pt(dcpe)(<i>cis</i> -dppe)	61.63 (61.59)	6.81 (6.95)	1043 (1013.9)
Pt(dcpe)(chiraphos)	61.82 (62.11)	7.02 (7.34)	^c
Pt(dcpe)(prophos)	61.44 (61.79)	6.94 (7.24)	^c
Pt(dppp) ₂	63.27 (63.00)	4.97 (4.87)	^b
Pt(dppe) ₂	^d		1148 (991.9)

^a In C₆H₆. ^b Insoluble. ^c Not measured. ^d Known compound.

closely approaches the tetrahedral angle. This effect should be observable in the P–Pt bond lengths of these compounds. A related effect was observed [6] for the complexes Pt(triphos)(L) (triphos = CH₃C(CH₂PPh₂)₃; L = PPh₃, PPh₂Me, P(OPh)₃). For these complexes the value of ¹J(P–Pt) for the triphos phosphorus atoms is unexpectedly small (2883–3096 Hz) but unexpectedly large for the unidentate ligand (5400–9150 Hz). This was thought to be the result of the greater s-character of the Pt–P bond of the unidentate ligand [6].

The mixed ligand complexes reported here should be useful for further studies on the effects of chelate ring size and substituents on the reactivity of platinum(0) complexes.

Experimental

All reactions were performed under an atmosphere of dinitrogen using standard Schlenk techniques. Phosphorus-31 NMR spectra were recorded on either a Bruker WP-60 spectrometer at 24.3 MHz or the Bruker WH-400 instrument of the South-Western Ontario High Field NMR Centre at 161.98 MHz. Chemical shifts are reported in ppm to high frequency of external 85% H₃PO₄. Platinum-195 NMR spectra were obtained on the WH-400 instrument. Chemical shifts are reported in ppm to high frequency of aqueous Na₂PtCl₄. NMR data are given in Table 1.

Infrared spectra were run on a PE-180 infrared spectrometer as Nujol mulls between KBr plates. Elemental analyses were performed by either Guelph Chemical Laboratories or Galbraith Laboratories. Analytical data are given in Table 2. Phosphine ligands were purchased from Strem Chemicals and were checked for purity by ^{31}P NMR before use.

The complexes PtCl_2L ($\text{L} = \text{dppm}$, dppe , dppp , dppb) and $\text{Pt}_2\text{Cl}_4(\text{Ph}_2\text{PC}\equiv\text{CPh})_2$ were prepared by literature methods [26,22] while $\text{PtCl}_2(\text{dcpe})$ (^{31}P NMR (CDCl_3): δ 64.1, $^1J(\text{P-Pt})$ 3577 Hz) was prepared by reacting stoichiometric amounts of $\text{PtCl}_2(\text{PhCN})_2$ and dcpe in chloroform. All the zerovalent complexes were prepared similarly, a typical preparation being as follows:

Preparation of Pt(dppe)(dppb)

The complex $\text{PtCl}_2(\text{dppe})$ (0.3 g, 0.45 mmol) was suspended in 20 ml of ethanol with dppb (0.192 g, 0.45 mmol) and the mixture refluxed until all the solid had dissolved (about 1 h). If necessary the solution was filtered to remove small amounts of undissolved solid. An aqueous solution of sodium borohydride (0.5 g, 13 mmol, in 10 ml H_2O) was then added dropwise resulting in the vigorous evolution of gas and the formation of a yellow precipitate. The resulting mixture was stirred for about 30 min. The yellow precipitate was then filtered, washed with water then ethanol and recrystallized from benzene/ethanol to give $\text{Pt}(\text{dppe})(\text{dppb})$ as a yellow powder (yield 0.34 g, 70%).

Abbreviations. $\text{dppm} = \text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2$; $\text{dppe} = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$; $\text{dppp} = \text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$; $\text{dppb} = \text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$; $\text{dcpe} = (\text{C}_6\text{H}_{11})_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_{11})_2$; $\text{dppbe} = o\text{-Ph}_2\text{PC}_6\text{H}_4\text{PPh}_2$; $\text{cis-dppe} = \text{cis-Ph}_2\text{PCH}=\text{CHPPh}_2$; $\text{dppa} = \text{Ph}_2\text{-PC}\equiv\text{CPh}_2$; $\text{arphos} = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{AsPh}_2$; $\text{chiraphos} = (2S,3S)\text{-Ph}_2\text{P-}(\text{CH}(\text{CH}_3))_2\text{PPh}_2$; $\text{propfos} = (R)\text{-Ph}_2\text{PCH}(\text{CH}_3)\text{CH}_2\text{PPh}_2$.

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